Journal of Physics and Chemistry of Solids 73 (2012) 204–208

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

The effects of different doping patterns on the lattice thermal conductivity of solid Ar

Kedong Bi [a], Yanyan Zhao [a], Yunfei Chen [a,*], Zhiyong Wei [a], Zan Wang [b], Yujuan Wang [a], Minhua Chen [a]

[a] Jiangsu Key Laboratory for Design and Manufacture of Micro-Nano Biomedical Instruments, School of Mechanical Engineering, Southeast University, Nanjing 211189, PR China
[b] School of Mechanical & Electrical Engineering, Henan University of Technology, Zhengzhou 450001, PR China

ARTICLE INFO

Article history:
Received 30 August 2011
Received in revised form
25 October 2011
Accepted 3 November 2011
Available online 7 November 2011

Keywords:
A. Nanostructures
D. Thermal conductivity

ABSTRACT

In order to investigate the effects of doping patterns on phonon transport, equilibrium molecular dynamics method is performed to calculate the lattice thermal conductivity of solid argon doped with krypton atoms in different geometrical distribution modes. Four different patterns are introduced through replacing Ar atoms with the same amount of Kr atoms in different volume and positions. The simulation results demonstrate that the impurity volume and distribution have significant effects on phonon transport in a crystal structure. The lowest thermal conductivity among the four doping patterns is achieved by introducing the impurity in a nanometer size cubic pattern distributed in the Ar matrix, which is roughly two times lower than that of pure argon at 17 K. The impurity strength on phonons is estimated through comparing the simulation results with those calculated from the Callaway model.

1. Introduction

The development of thermoelectric devices calls for materials with a high thermoelectric figure of merit *ZT*, which is characterized by $ZT=S^2\sigma T/\kappa$, where *S* is Seebeck coefficient, σ is electrical conductivity and κ is thermal conductivity. In order to enhance *ZT*, one must seek after materials with high *S*, high σ and low κ. Insulators, with relatively higher *S*, unluckily have poor electrical conductivity. On the contrary, metals, distinguished for their high σ, have relatively lower Seebeck coefficients. In addition, according to Wiedmann–Franz law, it is difficult to reduce the thermal conductivities of metals with no proportional reductions in their electrical conductivities in most cases. Fortunately, semiconducting materials, in which both phonons and electrons contribute to thermal conductivity, could be engineered to enhance their *ZT* through controlling the phonon and electron transport individually. Therefore, thermoelectric materials with high *ZT* can be achieved by reducing the phonon thermal conductivity, which is the majority of the whole thermal conductivity of semiconductors, without too much reduction in electrical conductivity.

Conventionally, alloying is a proven approach to reduce the phonon thermal conductivity, and bulk solid solution alloys of Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 are used as commercial thermoelectric cooling materials [1]. Quantum dot superlattices, which are regular arrays of semiconductor nanoparticles embedded in a semiconducting host material [2], have been confirmed with larger *ZT* values than those of their corresponding bulk alloys and are expected to be the most promising materials for thermoelectric applications [3]. For instance, 1% volume fraction of silicide nanoparticles can lead to a five-fold enhancement in the room temperature *ZT* of SiGe alloys [4]. The enhancement of *ZT* of these materials is attributed to the nature of their nanostructures with a high density of quantum nanodots, which could further suppress thermal conductivity [3,5]. There is strong evidence to show that, the strength of this effect in thermal conductivity of these nanostructures depends on several factors, including the sizes [4,6–8], densities [4] and distributions [9] of nanoparticles in them. It is found that [6], phonon scattering on quantum dots is an intermediate process between the point defect and boundary scattering, and the in-plane lattice thermal conductivity of a quantum dot superlattice becomes lower with the increase of the dot volume fraction and higher with the enlargement of the dot size when the dot size is a few nanometers. Nevertheless, recent reports [4,8] have shown that the optimal nanoparticle's size for the minimum thermal conductivity in these nanostructrues is always in the order of a few nanometers and the minimum value is not very sensitive to the nanoparticle's size. It is also demonstrated that a higher volume fraction of the nanoparticle leads to a lower thermal conductivity and a concentration of nanoparticles beyond a few percent might negatively affect the electron mobility of the material [4]. Ideally, acting as the additional phonon scattering centers, it is supposed

* Corresponding author. Tel.: +86 25 52090518; fax: +86 25 52090504.
E-mail address: yunfeichen@seu.edu.cn (Y. Chen).

0022-3697/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2011.11.001

that these nanoparticles should be uniformly distributed [10]. However, Monte Carlo simulation results show that the thermal conductivity of nanoparticle composite formed by distributing silicon cubic nanoparticles in a germanium matrix in staggered pattern is lower than that in random pattern [9]. The effects of different impurity distributions on the thermal conductivity of pure matrix have not been sufficiently studied yet, and the fundamental reasons for the thermal conductivity reduction in quantum dot superlattices are not fully understood either [7].

Motivated by those works mentioned above, the effects of four different geometrical arrangements of impurities on the thermal conductivity of argon crystal are investigated over the temperature range of 17–60 K using equilibrium molecular dynamics method in this work. The simulation results imply that a reasonable distribution of impurities is essential in order to produce a desired lower thermal conductivity.

2. Simulation techniques

Molecular dynamics (MD) simulation is an efficient tool to study heat transfer in nanoscale. In MD methods, positions and momentum space trajectories of all particles in a system are calculated by solving Newton equations of motion. Besides the interaction potential, no assumptions are needed to simulate heat transfer [11]. Equilibrium MD (EMD) and nonequilibrium molecular dynamics (NEMD) simulations are usually regarded as conventional MD methods to calculate the thermal conductivity of nanoscale materials. EMD method is more suitable to simulate the heat transfer in homogeneous materials than NEMD, and it is used in this work.

The widely accepted Lennard-Jones 12–6 (LJ) potential for bulk argon is employed in our model, which is read as:

$$u(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{1}$$

where ε is the well depth parameter and σ is the equilibrium separation parameter. r_{ij} signifies the distance between two atoms i and j. The cutoff radius, 2.6σ, is used to save time in the force calculations. Following the Green–Kubo formalism based on linear response theory, the lattice thermal conductivity of bulk solid argon is calculated by integrating the heat current correlation function, which is defined as

$$k = \frac{1}{3Vk_BT^2}\int_0^\infty \langle J(t)J(0)\rangle\, dt \tag{2}$$

where V, k_B and T are the volume of the simulated system, Boltzmann's constant and the system's absolute temperature, respectively. The heat current J is expressed as

$$J = \frac{1}{V}\left[\sum_i e_i v_i + \frac{1}{2}\sum_{i\neq j} r_{ij}(f_{ij}v_i)\right] \tag{3}$$

where v_i is the velocity of atom i and f_{ij} is the force acting on the atom i originating from the atom j. The total energy of atom i, e_i, is defined as

$$e_i = \frac{1}{2}m_i{v_i}^2 + \frac{1}{2}\sum_{j\neq i} u(r_{ij}) \tag{4}$$

Simulations are performed on the face centered cubic solid argon matrix; with the usual periodic boundary conditions imposed along the x, y and z directions. Key simulation parameters are shown in Table 1. To get reliable results, two million time steps are chosen in this work, which correspond to 10 ns for the heat flux autocorrelation integration. In our work, thermal conductivity is simulated over the temperature range of 17–60 K. The impurity is formed by replacing certain argon atoms with the same number of krypton atoms. Four different kinds of impurity arrangements are taken into account in this article, including (1) centralization doping, a certain quantity of argon atoms in the middle of the simulation domain are replaced by the same amount of krypton atoms; (2) monolayer doping, all impurities are arranged into one layer in the middle of simulation domain; (3) random doping, the impurities are distributed randomly; (4) cubic pattern doping, twelve cubic impurity units of the same size, each of which consists of six krypton unit cells, are evenly arranged in the simulation domain. The red regions in Fig. 1(a–d) present the distribution images of krypton atoms of centralization doping, monolayer doping, random doping and cubic pattern doping in the simulation domain. It should be pointed out that the impurity distribution image of the centralization doping in Fig. 1(a) is not exactly a cube, but all impurities are arranged together in the middle of simulation domain.

3. Results and discussions

To investigate the influence of the simulated domain's size on the results, the number of argon atoms in the simulated system ranges from 512 to 8192. The lattice thermal conductivities as a function of temperature for pure solid argon matrices with different sizes are calculated with a parallel computer system, which is shown in Fig. 2. As can be seen from Fig. 2, the simulation results agree well with previous experimental data [12] and NEMD simulation values [13]. Moreover, simulations on pure argon systems with different number of atoms display little difference from each other, which confirms that the finite size effects on the thermal conductivity is not evident. Due to the relatively shorter phonon mean free path in solid argon, the phonon–phonon scattering within the simulation domain is dominant, instead of the boundary scattering on phonons. This leads to the phenomenon that the thermal conductivity value is almost invariable with the increase of the simulation system size. So for convenience, thermal conductivities of all the distribution patterns of the impurity are simulated with the simulation domains including 8192 atoms in the following text. It can be also demonstrated from Fig. 2 that the thermal conductivity decreases with the increase of temperature. As temperature increases, more phonons in each vibration mode are excited. As a result, the collisions between the phonons become more intense, which is disadvantageous to the transport of energy.

Table 1
Simulation parameters.

Variable	Value	Variable	Value
Well depth of argon in LJ potential ε_1 (J)	1.67E−21	Equilibrium separation of argon in LJ potential σ_1 (m)	3.4E−10
Well depth of krypton in LJ potential ε_2 (J)	2.25E−21	Equilibrium separation of krypton in LJ potential σ_2 (m)	3.65E−10
Well depth for the interactions between Ar and Kr atoms in LJ potential ε_{12} (J)	$\sqrt{\varepsilon_1\varepsilon_2}$	Equilibrium separation for the interactions between Ar and Kr atoms in LJ potential σ_{12} (m)	$\frac{(\sigma_1+\sigma_2)}{2}$
Lattice constant (m)	5.3E−10	Time step	10 fs